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Strain-Induced Crystallization in Poly[methyl(3,3,3-trifluoropropyl)siloxane] Networks[1]

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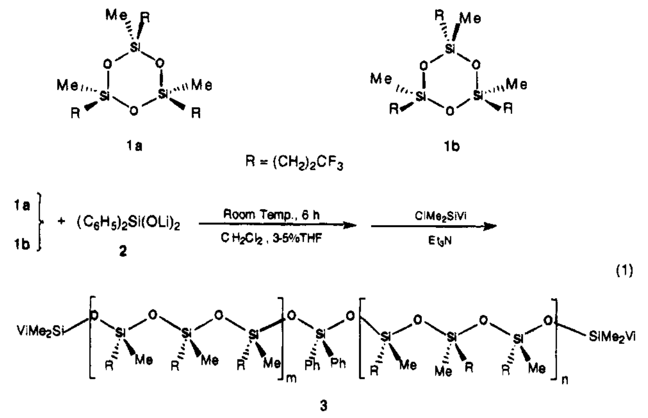
Strain-induced crystallization in elastomers provides unique combinations of mechanical properties not readily achieved with other types of reinforcement.[3] The phenomenon, important in natural rubber, depends on the capability of network chains to order quickly as they are stretched so they can crystallize. The crystallization process dissipates strain energy, and the formed crystallites act as temporary reinforcing particles which melt when the network is relaxed. The phenomenon is found in elastomer networks having chain flexibility combined with enough order prior to stretching so that there is a melting transition (T_m) at or slightly below the intended use temperature.[4] Unfortunately, the phenomenon is unknown in siloxane elastomer networks at normal use temperatures because of their very low or nonexisting T_m's. In the few cases where it has been reported, strain crystallization in poly(dimethylsiloxane) only occurred below −30 °C[5] and in poly(diethylsiloxane) below 0 °C.[6,7] Thus, in practice siloxane elastomer networks, which are inherently weak, require reinforcement with particulate fillers to build strength.[8]

We report here a successful strategy for introducing strain crystallization in siloxane networks where stereoregular repeat units compose the network chains. It is demonstrated with poly[methyl(3,3,3-trifluoropropyl)siloxane], **2** (PMTFPS), which is the basis of an important family of solvent resistant silicone elastomers. The method takes advantage of our recent finding that controlled amounts of stereoregularity can be introduced by polymerization of of *cis*- or *trans*-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane, **1a** and **1b** (*cis*- and *trans*-F_3), in mixtures of predetermined composition ranging from 0 to 95% *cis*-F_3.[9] Siloxane bond redistribution is suppressed during the polymerization and, depending on the amount of *cis*-F_3 present in the monomer, run lengths of isotactic triads are long enough that crystalline polymers are produced with T_m's approaching 45 °C. The polymerization is modified here with a bifunctional initiator so that reactive groups suitable for cross-linking can be introduced at both polymer ends, eq 1. This produces cross-linkable polymers of narrow molecular weight distribution with melting transitions adjusted to a range suitable for stress crystallization. Crucial factors are an efficient bifunctional initiator, thorough conversion of chain ends to reactive groups suitable for cross-linking and a cure system specific to the reactivity at the chain ends.

Experimental Methods. The initiator, dilithium diphenylsilanolate,[10] **2**, was prepared on a high vacuum line from a solution of 2.093 g (9.69 mmol) of dry diphenylsilanediol dissolved in 15 mL of 50 volume % purified benzene−THF containing 0.01 mL of styrene which served as an indicator. Just enough butyllithium was slowly introduced to the chilled solution so that it turned a persistent light yellow color. All volatile materials were then evaporated in the vacuum and replaced with 20 mL of purified dry benzene. The resulting solution was stored under dry nitrogen, but small amounts of precipitate usually formed after a few days which either settled to the bottom of the vessel or could be centrifuged. It was important that portions be taken only from the clear upper layer for initiating polymerizations or for assay by titration.



Details of the polymerization are essentially those of our previous procedure,[9] but modified here by initiating with **2**, terminating with chlorodimethylvinylsilane and using methylene chloride as the solvent with 3−5% tetrahydrofuran as a promoter. To ensure complete conversion of chain ends to vinyldimethylsilyl units, the crude polymers in methylene chloride were stirred with a 6-fold excess of vinyldimethylchlorosilane and equimolar triethylamine for 6 h. The methylene chloride solutions were washed with water, and the polymer was precipitated with excess methanol and then dried.

Cross-linking was by hydrosilylation with 10 g of polymer blended with 5 mg of 1-ethynyl-1-cyclohexanol, a transient inhibitor, and 10 mg of a proprietary platinum catalyst supplied by the Dow Corning Corp. The blend was mixed with a 50% excess (of SiH over vinyl end groups) of tetrakis(dimethylsiloxy)silane and degassed in a vacuum at room temperature, transferred to an aluminum mold, and further degassed. The mold and blend were then slowly heated and held at 135 °C for 1 h and then at 150 °C for an additional hour. Elastomers were aged at least 7 days before testing.

Results. Table 1 illustrates representative polymers made from monomer containing different amounts of *cis*-F_3 and properties of the corresponding networks after cross-linking. Molecular weight distributions were narrow and number average molecular weights were targeted to give a degree of polymerization of roughly 350 so that properties could be compared.

Crystallinity in the polymers increases as the amount of *cis*-F_3 present in the original monomer increases, as indicated by their T_m's and heats of fusion (H_f). The crystallinity persists in the corresponding elastomers, albeit at reduced levels. Polymers and elastomers made from pure *trans*-F_3 show no T_m. When the amount of *cis*-F_3 used in the original polymer is 48% or more, dynamic tensile breaking stresses of the elastomers are enhanced by factors of 13−21 over the elastomer from pure *trans*-F_3. Particularly distinctive are the high breaking strains in samples 2 and 3. This is commonly seen in natural rubber and other elastomers which

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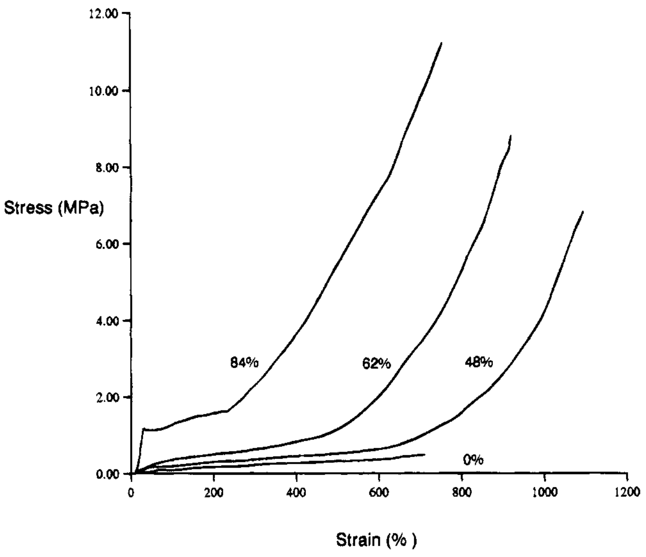

Figure 1. Dynamic stress–strain curves for PMTFS elastomers where the PMTFPS was made from monomer containing 0, 48, 62, and 84% *cis*-F_3, respectively. Samples tested at 24 °C and 50 mm/min.

Table 1. Properties of PMTFPS and the Corresponding Elastomers

	sample no.			
	1	2	3	4
cis-F_3 in monomer (%)	0	48	62	84
polymer yield (%)	86.1	90.5	83.0	90.0
polymer M_n ($\times 10^{-3}$)[a]	56.1	52.7	54.8	59.5
M_w/M_n[a]	1.07	1.05	1.13	1.06
T_g (°C) polymer[b]	−67.4	−69.0	−71.9	−66.1
T_g (°C) elastomer[b]	−65.1	−64.8	−63.4	−64.1
T_m (°C) polymer[b]		17.5	18.4	41.4
T_m (°C) elastomer[b]		−0.4	18.6	35.8
H_f (J/g) polymer[b]		6.4	9.6	12.0
H_f (J/g) elastomer[b]		7.4	7.7	11.1
breaking stress (MPa)[c]	0.517	6.80	8.48	11.15
breaking strain (%)[c]	708	1108	908	761

[a] By GPC in THF, polystyrene standards. [b] By DSc, 10 °C/min, samples cycled through their transitions twice prior to recording data. [c] Strained at 50 mm/min and 24 °C.

strain crystallize.[4] Partial reinforcement prior to straining is evident in sample 4 due to the presence of some crystallites; otherwise preexisting forms of reinforcement are absent from all samples.

The modulus at high strains for the elastomers progressively increases in dynamic stress–strain curves as the amount of *cis*-F_3 used in the preparation of the original polymer increases, Figure 1. This effect is absent when only *trans*-F_3 is used in the preparation of the original polymer. With the exception of the uppermost curve, the stress–strain curves show little or no hysteresis. Figure 2 shows equilibrium stress–strain curves plotted for diagnostic purposes in the semi-empirical Mooney–Rivlin format. This relates reduced stress (F^*) to strain ratio (α) according to:

$$F^* \equiv \frac{F/A}{\alpha - \alpha^{-2}} = 2C_1 - 2C_2\alpha^{-1} \qquad (2)$$

Where F is the restoring force, A is the cross-sectional area of the specimen prior to deformation, and $2C_1$ and $2C_2$ are constants. Normally, such plots approach linearity in elastomers lacking a reinforcing mechanism. This is seen in the elastomer where only *trans*-F_3 is used in the preparation of the original polymer and stereoregularity is essentially absent. The sharp upturns at 400–500% strain in the other examples in Figure 2; however, are indicative of strain-induced crystallization since other reinforcing mechanisms are absent.[11] Often minima appear just prior to the upturn, as seen in the upper curve of Figure 2. These have been interpreted in terms of orientation of the newly formed crystallites in the direction of the applied strain.[11]

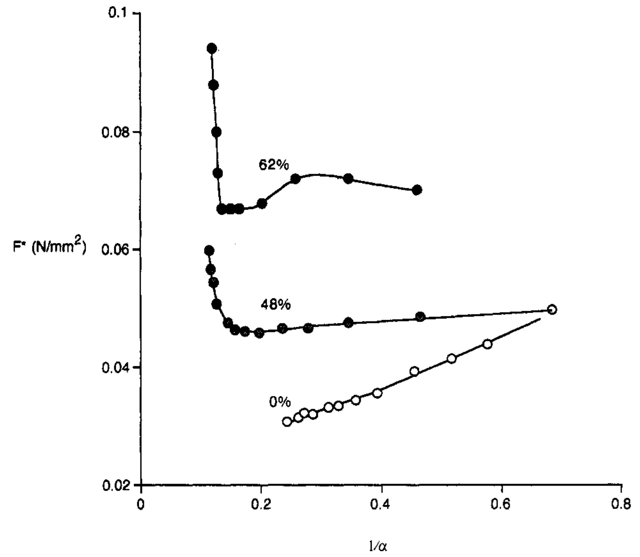

Figure 2. Reduced stress at equilibrium vs reciprocal strain at 24 °C for elastomers where the original monomer contained 0, 48, and 62% *cis*-F_3, respectively. Data points represent reduced stress after applying incremental strains and allowing the observed stress to relax to values where further change is negligible. See ref 11, p 13 for experimental details. For clarity data are shifted 0.03 N/mm^2 upward for the 48% curve and 0.04 N/mm^2 upward for the 62% curve.

The measurements in Figure 2 represent equilibrium values since points at a given strain could be reproduced after specimens were stretched to higher levels and then relaxed to the original strain. However, in the specimen where the original monomer contained 84% *cis*-F_3, preexisting crystallites resulted in more plastic rather than rubbery-like deformations. The nonequilibrium behavior therefore prevented expressing results in terms of eq 2 for this specimen.

Wide angle X-ray diffraction patterns of a specimen held at progressively increased strains confirm strain-induced crystallization, Figure 3. The relaxed specimen shows only a diffuse amorphous halo, but as strain increases this becomes a set of concentric rings and arcs and finally, at the highest strain, a pattern corresponding to a highly oriented fiber. We are presently characterizing the unit cell structure.

It should be pointed out that other authors have observed strain-induced self-reinforcement in cross-linked poly(diethylsiloxane) at room temperature.[6,7] The effect, while interesting, was uncharacteristic of genuine strain-induced crystallization and not as pronounced as the reinforcement seen here. They attributed their observations to mesophase formation, not to strain-induced crystallization. We feel the approach described here is a first example and that it can be extended to other stereoregular siloxane elastomer systems with equally rewarding results.

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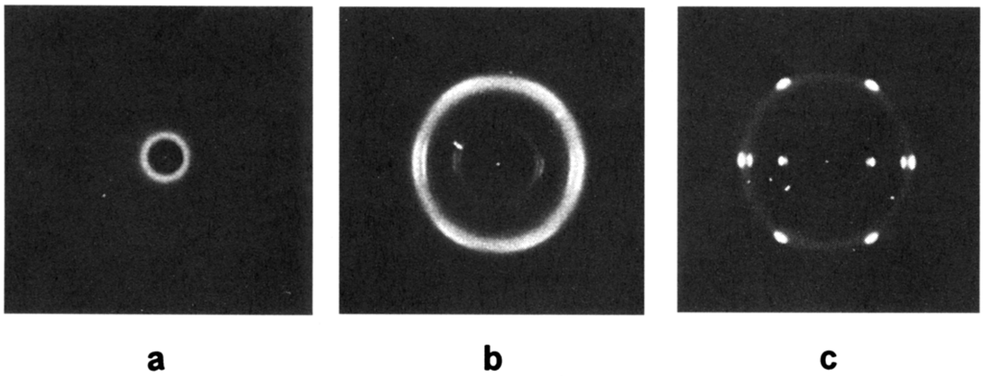

Figure 3. Wide angle X-ray diffraction patterns for the strained elastomer at 24 °C where the PMTFPS was made from monomer containing 62% *cis*-F_3: (a) at 0%, (b) at 500%, and (c) at 900% strains, respectively. Specimens were mounted in a special holder at the indicated strains and exposed for suitable times to a Cu Kα source (45 kV, 40 mA) from a Philips diffractometer fitted with a graphite crystal monochromator (1.5448 Å).

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References and Notes

(1) Presented at the American Chemical Society Award Symposium in Applied Polymer Science, March 1994, in honor of James E. Mark.

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